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Facile Esterification of Degraded and Non-Degraded Starch

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The iodine-catalyzed esterification (acetylation and propionation) and esterification with longer fatty acids of white dextrins (degraded starches) and "waxy potato" starch containing more than 95% amylopectin are reported. The degree of substitution can be finely tuned by a simple variation of the catalyst versus the amount of anhydroglucose units. Longer fatty acids can be readily converted using 1-methylimidazole as a solvent. The esterified carbohydrates are attractive for industrial purposes, offering high functionality, a broad variety of functional groups, high solubility, and a unique rheological behavior.

1. Introduction

Several new eco-friendly materials have the potential to replace conventional petroleum-derived materials and monomers, among them are natural polysaccharides.[1] Naturally occurring linear and (hyper)branched polysaccharides are amylose and amylopectin, respectively, the two components of starch. Starch is the most abundant storage reserve carbohydrate in plants; it is found in many different plant organs, including seeds, fruits, tubers, and roots, where it is used as a source of energy during periods of dormancy and regrowth.[2–5]

Therefore, starch seems to be a smart choice for designing new plastic materials with tunable properties.[6–9] However, the utilization of native polysaccharides for materials applications is limited since thermal decomposition takes place very easily. Moreover, their inherent moisture sensitivity leads to significant variations in their mechanical behavior with relative humidity. Thus, it is of fundamental importance to alter the used polysaccharides without modifying their biocompatible and biodegradable characteristics in order to reach desirable physical properties.

In particular, esterified polysaccharides have a tunable range of physical properties. For instance, modification of the starch OH groups with fatty acid esters (see **Scheme 1**), with the appropriate degree of substitution of about 1.5–3.0, imparts thermoplasticity and water resistance to the modified starch over the unmodified one. Modified starch-based materials are used in industry as glues, adhesives, and auxiliaries of a wide range of rheological and functional properties.

It was found that the properties of polysaccharide-based plastics are strongly dependent on the degree of modification as well as on the regioselectivity of the substitution. So far, sophisticated experimental techniques, solvents, or systems of solvents, were used to achieve homogeneous modification of the chosen polysaccharide. However, these techniques are expensive, typically use toxic solvents in highly alkaline conditions at high temperatures, are not viable for the large-scale industrial production of modified starches, and/or bear health risks when utilized.

Biswas et al. were able to show an elegant yet simple approach toward cellulose, starch, and other polysaccharides using acetic anhydride in the presence of a catalytic amount of iodine.[10] Iodine seems to be an excellent acylating reagent for both starch and cellulose as it activates the carbonyl group of acetic anhydride, making the latter more reactive toward the carbohydrates. This method was already used by several groups for very interesting cellulose modifications[11–13] and esterification of whole grain starches.[14–16]

In our current work, we studied the feasibility of this procedure in more detail for the esterification (acetylation, propionation, and esterification with longer fatty acids) of white potato dextrins (AVEDEX W80) and "waxy potato" starch containing more than 95% amylopectin (ELIANE)[17–19]—both are commercial carbohydrates used in various applications from food to paints.[20,21] Dextrins are frequently used in paper coatings as they readily form an adhesive paste when mixed with water. White dextrins, such as AVEDEX W80, are derived from starch by partial thermal degradation under acidic conditions.[22] The difference between white dextrins and other dextrins is that they can form a viscous paste in cold water, making them attractive for water-borne coatings.[23] ELIANE is a commercially available 100% amylopectin potato starch obtained via innovative classical breeding techniques.[24] Amylose has very low water solubility and amylose solutions are very unstable—amylopectin is highly soluble in water and forms stable solutions. ELIANE is therefore a very attractive high-molecular-weight[25] polysaccharide for stable high-content polysaccharide solutions and is at the moment mainly used in food applications.[26]

Both used carbohydrates are (highly) branched and hold a high amount of functional groups per molecule, which is especially attractive for industrial purposes[27] offering a high functionality, broad variety of functional groups, high solubility, and a unique rheological behavior.[28,29] The reported modification of these carbohydrates can be used to adjust their properties for specific

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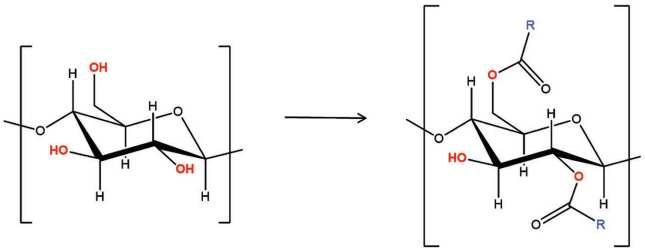

Scheme 1. Esterification reaction of polysaccharides.

applications, such as toughening additives and/or rheology modifiers.

2. Experimental Section

Already degraded amylopectin—white dextrins (AVEDEX W80) and pure amylopectin (ELIANE) were obtained from AVEBE and used without further purification. Iodine was provided by Boom and purified by sublimation twice. Acetic anhydride (Ac_2O) (≥99.0%) and propionic anhydride (Pr_2O) (≥96.0%) were provided by Fluka; butyric anhydride (Bu_2O) (≥98.0%), hexanoic anhydride (97%), heptanoic anhydride (96%), nonanoic anhydride (≥98.0%), dodecanoic anhydride (≥98.0%), sodium thiosulfate (NaS_2O_3) (≥98.0%), and dimethyl sulfoxide (DMSO) (99%) were provided by Sigma-Aldrich. Ethanol (≥99%) was purchased from Merck KGaA and used without further purification.

^{1}H NMR spectra were recorded on a Varian VXR spectrometer (400 MHz). The reported chemical shifts were referenced to the resonances of the residual solvent or tetramethyl silane (TMS).

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) measurements were conducted on a Bruker IFS88 FT-IR spectrometer. For each sample, 128 scans were performed.

Thermal transitions were measured by differential scanning calorimetry (DSC) on a TA-Instruments Q1000. The heating and cooling rates were 10 °C min^{-1}. To remove the remaining water and solvents in the polymer, the tested samples were first heated up to 100 °C at 10 °C min^{-1}, maintained at this temperature for 5 min, and then cooled down to room temperature before the standard DSC measurement.

Thermal stability was characterized by thermal gravimetric analysis (TGA) on a PerkinElmer thermogravimetric analyzer TGA7 under a nitrogen environment. The scan rate was 10 °C min^{-1}. To remove the remaining water and solvents in the polymer, the tested samples were first heated up to 100 °C and then maintained at this temperature for 0.5 h before the standard TGA measurement.

The gel permeation chromatography (GPC) system set-up (Agilent Technologies 1260 Infinity) from PSS (Mainz, Germany) consisted of an isocratic pump, auto sampler without temperature regulation, an online degasser, an inline 0.1 µm filter, a refractive index detector (G1362A 1260 RID Agilent Technologies), viscometer (ETA-2010 PSS, Mainz), and MALLS (SLD 7000 PSS, Mainz). WinGPC Unity software (PSS, Mainz) was used for data processing. The samples were injected with a flow rate of 0.5 mL min^{-1} into a Suprema pre-column and three Suprema size exclusion chromatography (SEC) columns 100, 3000, and 3000, which were also purchased from PSS. The columns and the detectors were held at 50 °C. A standard pullulan kit (PSS, Mainz, Germany) with molecular weights from 342 to 805 000 Da was used to generate a universal calibration curve, in order to determine the hydrodynamic volume from the elution volume.

2.1. Esterification Reaction

In a round bottom flask, equipped with a magnetic stirring bar, 2 g (11.1 mmol) AVEDEX W80 were dissolved in 1.57 mL (16.6 mmol) acetic anhydride. After adding 120 mg of iodine, the mixture was heated at 100 °C for 10 min. After cooling down to room temperature, the mixture was treated with a saturated solution of sodium thiosulfate. The mixture color changed from purple-brown to colorless, indicating the transformation of iodine to iodide. The mixture was poured into 100 mL of ethanol and stirred for 30 min. After filtration and washing with a 90/10 solution of EtOH/H_2O the final product was dried in vacuo. This reaction was modified in several ways, regarding the Ac_2O/AGU (anhydro glucose unit) ratio, reaction time, temperature and the acylating agent (acetic/propionic anhydride), amount of catalyst, precipitating agent and washing agent. All obtained esterified carbohydrates were analyzed via IR and NMR; selected samples were analyzed via DSC, TGA, and GPC.

For the propionation of AVEDEX W80 the mixture was heated at 110 °C for 15 min (rest of the procedure is not changed).

For the acetylation of ELIANE the mixture was heated at 110 °C for 15 min (rest of the procedure is not changed).

For the propionation of ELIANE the mixture was heated at 115 °C for 20 min (rest of the procedure is not changed).

2.2. Acylation with Longer Fatty Acids (Anhydrides)

1g of polyol was dissolved in 33 mL 1-MIZ under stirring. A heat gun was used to accelerate the process. After obtaining a clear solution, it was cooled down to 0 °C in an ice bath. The right amount (dependent on the desired D.S.) of anhydride was added dropwise to the solution via a syringe. The solution was stirred after the addition of the anhydride for a defined period of time and samples were taken every 20 min to control the kinetics and finish the reaction after the desired D.S. is obtained. The mixture was precipitated in a non-solvent (H_2O), the modified carbohydrate collected in a centrifuge and the supernatant filtered to collect loose parts from the solution. The white powder was dried in a desiccator under P_2O_5 and recrystallize with the help of acetonitrile if necessary.

3. Results and Discussion

Acetylation of polysaccharides with acetic acid or acetic anhydride has been known for a long time. Although the products are very useful, the processes involved in acetylation are sometimes not environmentally friendly and may need solvents such as methylene chloride or extreme conditions with sulfuric or perchloric acid as a catalyst. It was found that acetic anhydride in the presence of a catalytic amount of iodine is an

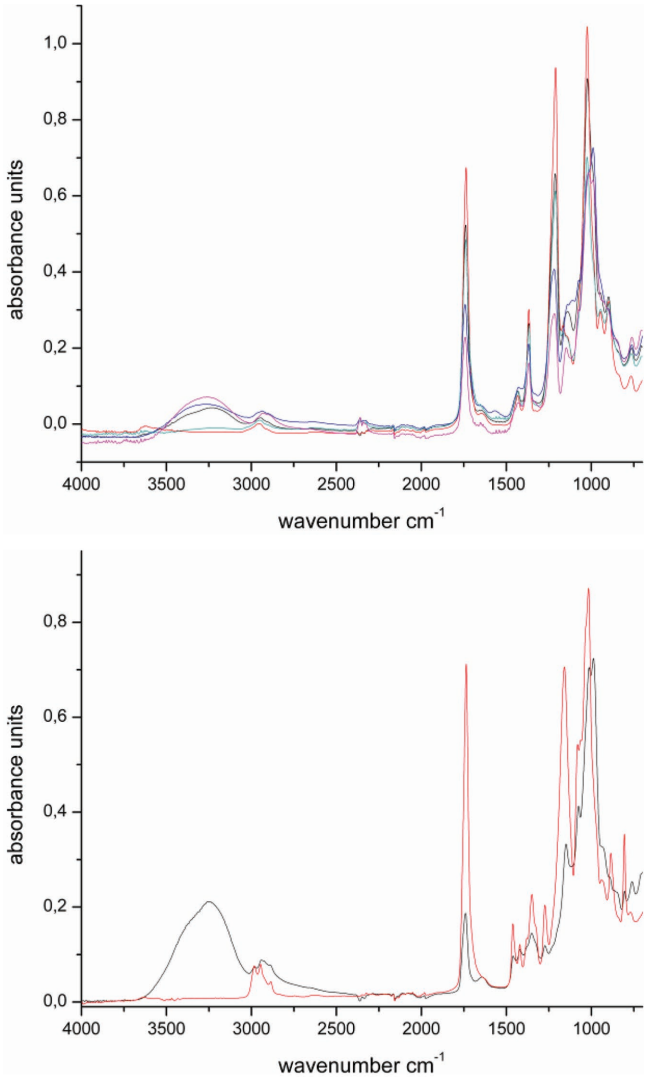

Figure 1. FT-IR spectra of (top) acetylated AVEDEX W80 (DS = 0.7; 0.8; 1.5; 2.0; 2.8), (bottom) propionated AVEDEX W80 (DS = 0.5; 2.8).

excellent acylating reagent as it activates the carbonyl group of acetic anhydrides, making the latter more reactive.

The iodine-catalyzed acylation and propionation (see Scheme 1) up to a DS of 3 (full esterification) of AVEDEX W80 proceeded readily as proven by FT-IR spectroscopy (see **Figure 1**). The acylation is straightforward; the propionation requires a slight increase in reaction temperature and time.

The iodine-catalyzed acylation and propionation of ELIANE required a further slight increase in reaction temperature and time, together with an increase in acylating agent. This is due to the higher molecular weight of the amylopectine in ELIANE as compared to AVEDEX W80. Nearly fully acylated/propionated ELIANE could be synthesized (see **Figure 2**).

There are several ways to determine the DS of the modified carbohydrates. In our case, ^{1}H NMR proved to be the fastest and most reliable method. Comparing the area under the glucose-protons peak with the area under the acetate/propionate peaks results in the average DS—see **Figure 3** for sample spectra and calculations.

Due to the high molecular weight of the ELIANE amylopectin and the resulting complications in characterizing the products, all further characterization techniques are reported exclusively for AVEDEX W80 but are analogous for ELIANE.

The acetylation of AVEDEX W80 was successfully scaled up, resulting in the possibility to reduce/increase the amount of catalyst. In addition, it allowed us to do a series of experiments in which all reaction conditions besides the amount of catalyst are kept constant, and the influence of the amount of catalyst on the DS can be studied (see **Figure 4**). It becomes obvious that the DS can be finely tuned by a simple variation of the catalyst versus the amount of anhydroglucose units.

The molecular weight of the pristine AVEDEX W80 and acetylated AVEDEX W80 was determined using DMSO-GPC to check for possible carbohydrate cleavage during the esterification reaction.[30,31] The results in **Figure 5** and **Table 1** confirm that the polysaccharide backbone is not degraded during this reaction. The obtained molecular weight is in accordance with the molecular weight stated by the supplier. In addition, the

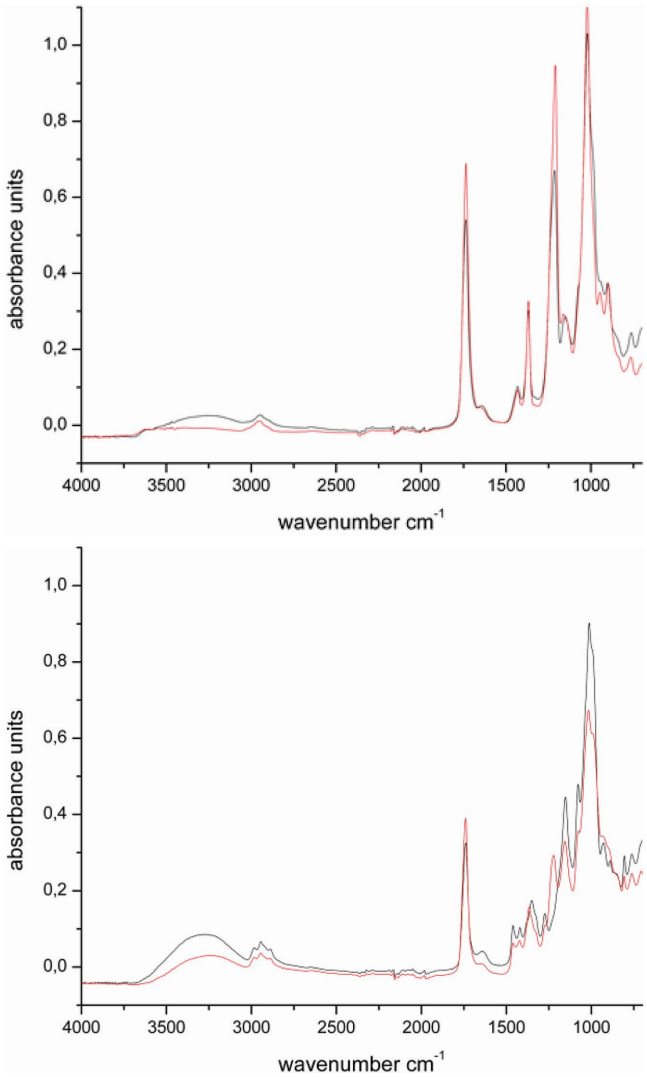

Figure 2. FT-IR spectra of (top) acetylated ELIANE (DS = 1.8; 2.84), (bottom) propionated ELIANE (DS = 0.9; 1.2).

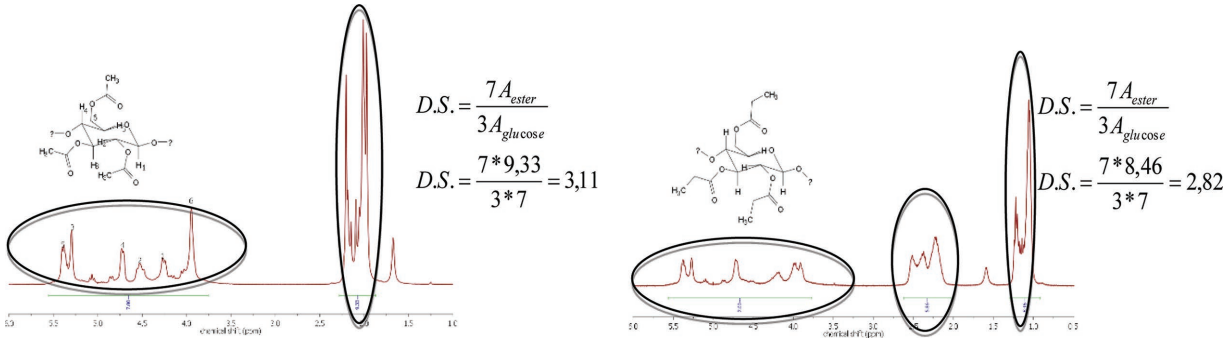

Figure 3. Calculation of DS from ^{1}H NMR spectra of AVEDEX acetate (left) and AVEDEX propionate (right).

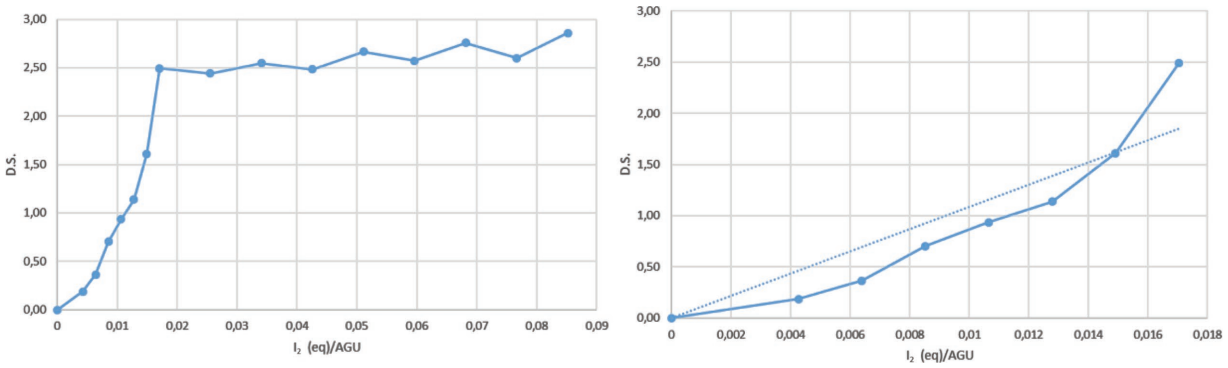

Figure 4. Tunability of the degree of substitution via variation of the amount of catalyst.

molecular weight of the higher DS samples (DS 2.76 and 2.86) is significantly higher than the molecular weight of the low DS (0.19) sample, proving the success of the acetylation reaction.

The thermal properties of pristine and acetylated AVEDEX W80 with different DS were compared using TGA and DSC analysis, respectively. From the TGA analysis in **Figure 6**, it is obvious that up to 250 °C, the stability of the acetylated carbohydrates is increased in relation to the unmodified AVEDEX W80. Comparing samples of different DS leads to the conclusion that the higher the DS, the more stable the carbohydrate is. The increase in thermal stability is a consequence of the lower amount of remaining hydroxyl groups in AVEDEX W80 after the acetylation. Furthermore, the increase in molecular weight and in covalent bonds due to the acetylation enhances thermal stability. With the introduction of ester groups into the carbohydrate, a glass transition is introduced into the material, indicating a transformation into an amorphous material. With increasing DS, the T_g is decreasing as the introduced flexible side chains function as a plasticizer in the system.

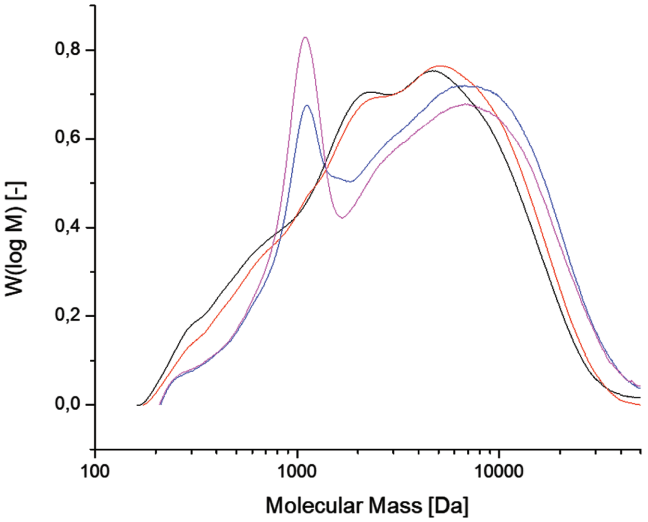

Figure 5. GPC elugrams of (black) pristine AVEDEX W80 and acetylated AVEDEX W80 with DS of 0.19 (red), 2.76 (blue), and 2.89 (magenta).

Table 1. Molecular characteristics of pristine AVEDEX W80 and acetylated AVEDEX W80 with different DS.

	AVEDEX W80	DS 0.19	DS 2.76	DS 2.86
M_n	1592	1789	2293	2117
	1585	1740	1961	1825
$M_{n,average}$	1589	1765	2127	1971
M_w	5237	5604	7518	6926
	5148	5519	6791	6502
$M_{w,average}$	5193	5562	7155	6714
M_z	11 430	11 611	17 170	15 690
	11 056	11 289	15 212	14 845
$M_{z,average}$	11 243	11 450	16 191	15 268

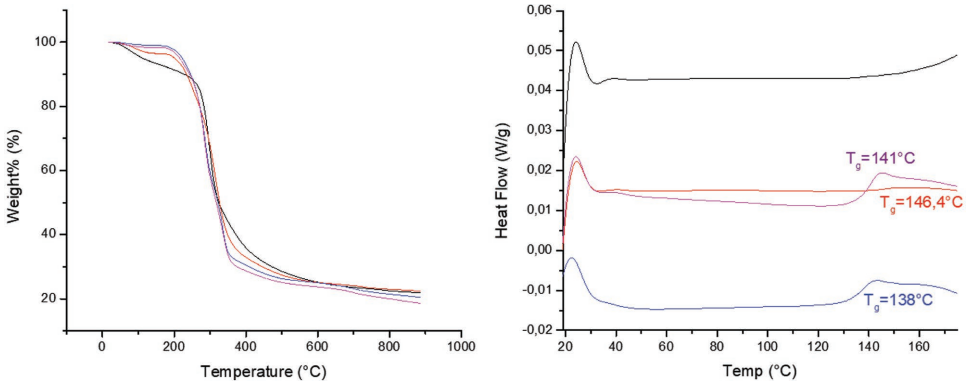

Figure 6. (left) TGA analysis and (right) DSC analysis of (black) pristine AVEDEX W80 and acetylated AVEDEX W80 with DS of 0.19 (red), 2.76 (blue), and 2.89 (magenta).

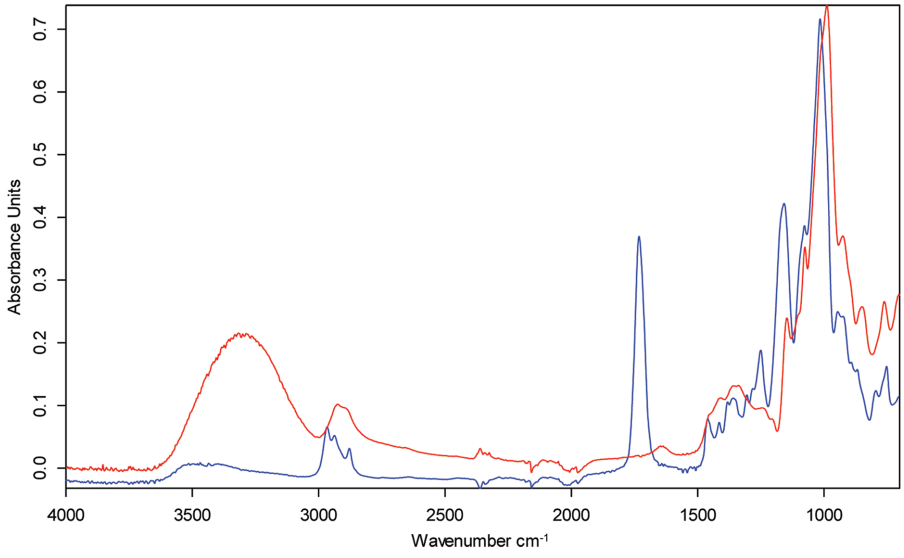

Figure 7. FT-IR spectrum of pristine AVEDEX W80 before (red) and after (blue) esterification with butyric anhydride (DS 1.87).

It is not possible to esterify carbohydrates with longer fatty acids than propionic acid (anhydride) with the above-mentioned method. To achieve this, the procedure has to be slightly modified: the carbohydrate is dissolved in 1-methylimidazole at elevated temperatures and reacted with the anhydride of the appropriate acid at 0 °C; precipitation and recrystallization reveal the final product. With this method, it is possible to esterify carbohydrates with butyric anhydride and longer fatty acids. The FT-IR spectrum of the product of the esterification using butyric anhydride and a targeted DS of 2.0 is shown in **Figure 7**. Clearly visible is the newly formed ester peak at around 1730 cm^{-1} and the disappearance of the hydroxy peak around 3200 cm^{-1}. The kinetics of the reaction was followed by ^1H NMR (see Figure S1, Supporting Information). The final DS (1.87) is close to the desired DS (2.0), which was set at the beginning of the experiment by the amount of anhydride used. The final product is a white powder, proving that no furfural was formed during this reaction. The kinetic studies show that the reaction is already finished after 30–60 min reaction time (see **Table 2**). This should be considered for further reactions, to prevent unnecessary degradation of the carbohydrate due to extended reaction times.

Longer fatty acids can be readily converted in this reaction as well, the ^1H NMR spectra of the products of the esterification reaction of AVEDEX W80 with hexanoic anhydride, heptanoic anhydride, nonanoic anhydride, and dodecanoic anhydride can be found in the Supporting Information.

4. Conclusions

We developed and studied the details of esterification reactions to esterify low (AVEDEX W80) and high (ELIANE) molecular weight branched polysaccharides up to a DS of 3. A reaction using acetic anhydride as an acylating agent proceeded the fastest. Propionic anhydride requires a longer reaction time, an increased temperature, and a higher amount of acylating agent. An esterification method for fatty acids longer than C > 3 was developed using 1-methylimidazole.

In all reactions, the desired degree of substitution can be achieved using the right amount of catalyst versus the amount of anhydroglucose units.

A very important feature of this reaction is the fact that the esterified material does not undergo a color change due to the mild reaction conditions. This can be very important for various industrial applications, such as coatings, films, etc.

Table 2. Kinetics of esterification reaction of AVEDEX W80 with butyric anhydride.

Time [min]	DS
20	1.51
30	1.75
60	1.87
90	1.87

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbohydrates, degree of substitution, esterification, iodine catalysis, starch

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